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Development of Oxygen Transport Membranes for Coal-Based Power Generation

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Abstract

Praxair is developing an Advanced Zero Emission Coal Fired Power Plant (Advanced Power Cycle) that enables carbon capture and sequestration (CCS) at a "levelized" cost of electricity below the U.S. Department of Energy's target for CO_2 capture from coal fired power plants. The power cycle utilizes a gasifier, partial oxidation units, power recovery turbines and an oxygen fired boiler to yield a process that meets the DOE's goal of <35% increase in cost of electricity with CCS. Through the use of Praxair's reactively driven Oxygen Transport Membrane (OTM) technology, the parasitic load of the oxygen supply system to both the partial oxidation reactors and boiler is reduced by approximately 75%. The Advanced Power Cycle [1] uses coal gasification to produce a gaseous fuel that is then combusted in an oxygen fired supercritical boiler. Low cost oxygen is made available by integrating Praxair's OTMs into the boiler and, depending on the gasifier selected, into a post gasification partial oxidation system to convert tars and methane to CO and hydrogen. Praxair has completed a detailed techno-economic analysis of the performance of the Advanced Power Cycle (APC) and achieved significant breakthroughs in the OTM architecture and gas separation layer chemistry to achieve the commercial flux targets under phase 1 of a cooperative research agreement [2] with the United States Department of Energy (DOE). Phase 2 of this agreement, currently underway, is focused on developing a detailed cost estimate of key components of the cycle as well as developing fabrication cost estimates of the membranes. While the APC is targeted at coal based CCS, the key components of the APC can offer benefits to integrated gasification fuel cell cycles, natural gas combined cycle plants as well as other processes. These additional processes represent opportunities to demonstrate key components of the APC prior to demonstrating the technology in its entirety. These opportunities not only allow investment dollars to be leveraged for additional benefits but also allow critical performance and reliability to be gained at commercial scale in an industrial environment – a critical hurdle that must be crossed for any new technology to be implemented at utility scale. Praxair is encouraged by the progress made to date and believes that great progress has been made in the area of materials and cycle development. The newly developed materials and membrane architecture have met commercial flux targets while demonstrating robust performance. The APC holds great promise to address the needs of CCS, while minimizing the cost of compliance.

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1. Process Cycle

During the initial phase of the program, Praxair developed and evaluated a number of different process cycles. Through a series of feasibility and techno-economic analyses one cycle was selected to result in the smallest increase in the cost of electricity when compared with an air fired pulverized coal plant. The process cycle that was selected is illustrated in Figure 1. The concept utilizes a gasifier that is fed with oxygen from a conventional air separation unit (ASU). The gasifier is selected such that it achieves high carbon conversion with minimal oxygen. After particulate cleanup, the syngas is reacted in an OTM partial oxidation (POx) reactor to raise the temperature prior to expansion through a power recovery turbine (PRT). Figure 1 shows a series of two POx/PRTs to maximize the efficiency of power recovery. After expansion to slightly above atmospheric pressure the synthesis gas is fed to the OTM boiler. In the OTM boiler, synthesis gas reacts with oxygen separated from air via OTM devices. The conceptual design of the boiler has OTM elements interspersed with steam tubes such that the radiant heating from the OTM elements supplies the energy to the steam tubes. While the OTM provides low cost oxygen for the bulk of combustion, the incremental OTM area required to provide the final oxygen to complete combustion comes at a cost higher than that of conventional oxygen production. Therefore, the final 10 – 20% of the oxygen required to complete combustion is supplied from the conventional ASU (although not shown in Figure 1). This is due to the decrease in oxygen flux with lower concentrations of fuel species. The process as illustrated in Figure 1 is designed to allow the optimization of the overall cost of oxygen by balancing it between conventional cryogenic ASU and advanced OTM methods. After the fuel is completely oxidized with externally supplied O_2, the flue gas will pass through a convective section of the boiler for further steam generation and boiler feed water preheating. The flue gas exiting the FGD scrubber is compressed to >2000 psia and purified to >95% purity for sequestration or enhanced oil recovery (EOR).

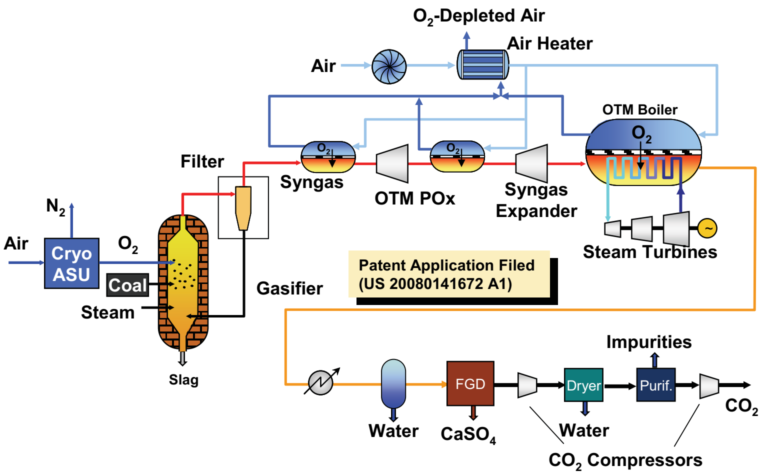

Figure 1. Process for Integration of OTM into Power Generation Cycle with CO_2 Capture

Although the OTM power cycle uses a gasifier at the front end of the process, its CO_2 capture characteristics are similar to an oxy-combustion process. Table 1 shows a comparison of the key features of the OTM power cycle, an IGCC power cycle and an oxyfuel fired boiler cycle. If CO_2 capture is required from an IGCC-based power plant, the syngas from the gasifier must be shifted to maximize the hydrogen concentration using water gas shift. The shifted syngas is cooled to near ambient temperature where an acid gas recovery unit removes sulfur compounds and CO_2 from the cooled syngas stream and hydrogen is sent to a combined cycle section for power generation. A significant amount of fuel energy is lost as the coal is transformed into hydrogen. A report published by DOE/NETL

[3] shows that the efficiency of an IGCC plant with CO_2 capture will range from 31.7% (HHV) to 32.5% (HHV) depending on the type of gasifier used.

Table 1: Comparison of features of APC, IGCC and Oxyfuel power cycles

	APC	IGCC	Oxyfuel
Gasifier	Yes	Yes	No
Syngas Expander	Yes	Yes/No	No
Shift Reactor	No	Yes	No
Acid Gas Recovery (e.g. Selexol)	No	Yes	No
H_2 Combustion Turbine	No	Yes	No
Steam Generation Unit	OTM Boiler	HRSG	Oxyfuel Boiler
Oxidant for Combustion	Oxygen	Air	Oxygen
Pre-Combustion CO_2 Capture	No	Yes	No
Oxy-Combustion CO_2 Capture	Yes	No	Yes
Power Production from Major Units			
Combustion Gas Turbine	0%	62%	0%
Syngas Expander	18%	1%	0%
Steam Cycle	82%	37%	100%

In the OTM process, there is no loss of energy associated with syngas conditioning for CO_2 and sulfur removal. Laboratory scale tests have demonstrated the ability of the membranes to survive in atmospheres with up to 1% of H_2S and COS. Overall, the OTM process is projected to achieve 37.2% (HHV) efficiency [4] when coupled with an ultra supercritical steam cycle. This is 4.7 to 5.5 percentage points higher than the efficiency of an IGCC plant with CO_2 capture [3] and within 2.5 percentage points of a conventional air fired PC Boiler without CO_2 capture. In the IGCC process, CO_2 must be separated using solvents such as selexol, rectisol or other amine. In the OTM process, the CO_2-rich stream is generated in the OTM boiler similar to a conventional oxygen-fired PC boiler. In IGCC, about two thirds of the power is generated by the combustion turbines with the remaining third generated in the steam cycle. In the OTM power cycle, more than 80% of the power is generated in the steam cycle and the balance of power is generated by syngas expanders. Final purification of CO_2 in the OTM process is similar to that of a conventional oxy-combustion process. Overall, the OTM power cycle shares more features with the conventional oxy-combustion process than that of an IGCC process.

2. Techno Economic Analysis

A detailed techno-economic evaluation of the APC was performed for 6 cases to determine the cycle efficiency and cost of electricity (COE) in 2008 dollars. The six simulated cases investigate the effect of 2 main parameters: steam cycle complexity (super critical, ultra-supercritical and advanced ultra-supercritical) and type of sulfur recovery unit (flue gas desulfurization and warm gas cleanup unit). For each of the 6 cases evaluated, the sensitivity of COE to coal price was evaluated using three coal prices. The results of this analysis are shown in Table 2. Thirteen of the eighteen scenarios satisfy the DOE goal of less than 35% increase in COE. These cases are highlighted in green in Table 2. Higher coal price favors the APC COE (relative to other processes, e.g. IGCC) due to the high efficiency enabled by utilization of OTM technology in the process cycle.

Table 2: Comparison of OTM cases with Air PC base case (cost basis for all cases March, 2008)

		OTM FGD Cases			OTM WGCU Cases			Air-PC Case
Case		1 SC	2 USC	3 Adv USC	4 SC	5 USC	6 Adv USC	Praxair/DOE No CCS SC
Net Efficiency (HHV) (%)		36.3	37.2	39.7	36.6	37.4	39.9	39.7
Plant Cost ($/kW)		2,894	2,887	2,997	2,872	2,863	2,956	1,908
	Coal Price ($/MMBtu)							
Increase in COE over Reference	1.8	39.4%	38.4%	39.7%	36.0%	35.0%	36.2%	
	3	34.9%	33.8%	33.8%	32.0%	30.8%	30.6%	
	4	32.1%	30.8%	30.0%	29.4%	28.0%	27.1%	

In comparison to other power cycles that enable carbon capture and sequestration (CCS), the APC has a uniquely low cost of CO_2 removed and avoided due to a relatively low COE, a high net cycle HHV efficiency, and high CO_2 capture efficiency. Additionally, the high net cycle HHV efficiency results in low operating cost making these units more likely to operate as base loaded units as opposed to other CCS equipped power plants with high operating costs that would be lower on the dispatch list.

3. Materials Development

The structural, chemical and mechanical stability of OTM materials at high temperatures and in reducing environments is critical to the reliability of the OTM system. In the 1998 – 2003 time frame, ceramic membrane failures were prevalent during heating, cooling, thermal cycling, and changes in fuel composition, due in part to mechanical strength deficiencies and to chemical and thermal expansion mechanisms associated with the single phase pervoskites that were utilized. Recognizing the importance of reliability and the challenges in managing this with a single phase perovskite system, Praxair redesigned the OTM architecture using a combination of layers and materials to address the known failure mechanisms and the functional requirements of the membranes. In 2005 a breakthrough in the materials development was achieved. With the new materials set, the failure rate in small laboratory scale reactors dropped to near zero. However, while the reliability of the system improved dramatically, the oxygen flux performance suffered. Techno-economic analyses indicated that a performance improvement of at least 2x was required to achieve economic targets. A detailed analysis of the rate limiting steps indicated that improvements in mass transfer through the porous support and fuel oxidation at the anode surface would have the biggest impact on membrane performance. Significant progress was made in both of these areas as illustrated in Figure 2 where the combination of improved mass transfer and improved fuel oxidation result in nearly a 4x improvement in oxygen flux. With the improvements in fuel oxidation and architecture of the porous support and the associated improvement in performance, some failures were initially observed when the fuel flow was turned off at the completion of a test. More recently, high performance, single tube OTM structures have been demonstrated to maintain performance and structural integrity after several full thermal and chemical cycles in laboratory scale reactors. Failure analysis has indicated that failures are more often related to the laboratory scale seal technology used in the test stands. Not withstanding this identified issue, the OTM tubes continue to be robust during heat up in air and rapid addition of fuel. These characteristics were not achieved with the original OTM material set (e.g. single phase perovskites) utilized in the 1998 – 2003 timeframe.

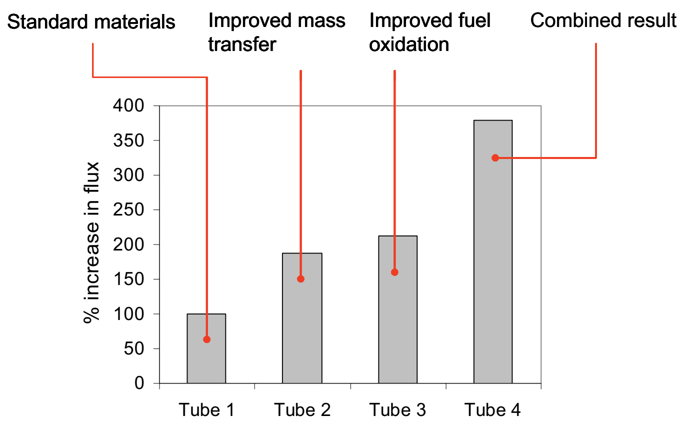

Figure 2: Membrane performance for individual and combined improvements in porous support and fuel oxidation (Tube 1: Standard support, Tube 2: Improved support, Tube 3: Improved fuel oxidation, Tube 4: Improved support & fuel oxidation).

4. Synergies with Other Technologies

While the focus of Praxair's efforts under the DOE cooperative agreement are on the advanced power cycle, key components of the process cycle have benefits in other areas as well. These areas include:

Integrated Gasification Fuel Cell (IGFC) power cycle
OTM devices could be utilized in multiple locations in the process cycle currently under consideration to reduce the parasitic load of the oxygen on the overall process. This would result in an increment boost in net power output and overall cycle efficiency.

Process heating furnaces in refineries and chemical plants (e.g. crude heaters, ethylene crackers, etc.)
The CO_2 Capture Project [5] is currently studying different solutions for capturing CO_2 emissions from process heaters within refineries. As CCS regulations extend beyond power production, the OTM boiler approach would facilitate oxyfuel combustion with a significantly lower cost of oxygen.

Natural gas combined cycle power plants
Based on a preliminary evaluation, the benefits of integrating OTM elements into a NGCC include < 35% increase in COE for CCS, 100% CO_2 capture; < 1ppm NOx emission and >20% reduction in cost of capturing CO_2 compared to post-combustion.

5. Development Roadmap

With the progress that has been made on materials and membrane performance, Praxair is in the process of forming strategic alliances with firms that will continue the development of the technology in a collaborative effort. The near term goal of the joint effort will be to develop an OTM module that is conceptually similar to an SOFC stack. The OTM module then becomes the building block for larger scale systems. It is anticipated that the next phase of the project will run through 2015 and will culminate in a robust, reliable, module design that has been proven in pilot scale test equipment in both a partial oxidation mode and a combustion mode. Follow on efforts will focus on scaling the system size thereby demonstrating the scalability of the system and positioning the technology for future commercial scale demonstrations.

6. Conclusions

Praxair is encouraged by the progress made to date and believes the APC holds great promise to address the needs of CCS while minimizing its cost. The work completed over the past 6 years under the DOE cooperative agreements has led to the development of a robust material set that is capable of surviving in an industrial environment. The materials have demonstrated the ability to survive transients with no special precautions. In addition to continuing to improve the performance of the materials, future work will focus on integrating and packaging the membranes into reactors and long term testing of these systems. We look forward to continuing our cooperation with the DOE to scale up this technology and deliver a cost effective solution for carbon capture and sequestration for fossil fuel fired power plants.

7. Disclaimer

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